YEARLY PROGRESS REPORT

Project Title: Inert Anode Metal Life in Low Temperature Aluminum Reduction Process

Covering Period: October 1, 2001 through September 30, 2002

Date of Report: January 31, 2003

Recipient: Northwest Aluminum Technologies
3313 West 2nd Street
The Dalles, OR 97058

Award Number: DE-FC07-98ID13662

Subcontractors: Goldendale Aluminum Company, CSIRO

Other Partners: Oregon State University, LLNL

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Project Objective: The objectives are to investigate a new Low Temperature Electrolysis (LTE) aluminum smelting process, and develop the total system with the goal of commercialization. These objectives include the design and implementation of a 5000 ampere cell pilot plant.

Background: The LTE systems approach differs significantly from the traditional Hall-Heroult process for primary aluminum production. Differences include nonconsumable (inert) anodes that produce oxygen rather than carbon oxides as offgas, wetted cathodes, vertical electrode arrangement, reduced operating temperature, slurry electrolyte, reduced energy intensity, lower cost, and smaller cell footprint.

In order to progress towards the project objectives, work was undertaken at the lab scale to address the various unique aspects of the LTE process. Initial lab scale testing utilized small, 10 ampere, test stands to

survey anode compositions, electrolyte compositions, and operating conditions. Work with larger 200-300 ampere cells was begun to address issues of scale-up and to facilitate long-duration tests. This is important not only as a precursor to scale-up operations, but also because post-test characterizations of the system components complement data gathered earlier in the program with shorter tests.

Currently the emphasis is upon long-duration tests at the 200-300 ampere scale, and design and fabrication of 5000 ampere pilot cells. Additional ongoing emphases include modeling activity directed both towards cell/process design and fundamental aspects of electrode performance, experimental support of the modeling activity, investigation of various process control techniques for their utility with LTE, metallurgical properties of anode alloys, fundamental studies of anode function, and laboratory studies of alternative designs and process conditions.

Status:

The status is best summarized with discussions of four areas of focus. These are laboratory tests, 200A cell tests, metallurgical studies, and 5kA cells.

Areas of focus

The laboratory tests address the ongoing needs for fundamental characterization of the system components, and for evolution of system process control. The fundamental studies include characterizations using scanning electron microscope (SEM) and microprobe methods, determinations of physical properties, and electrochemical studies. The process related work addresses evolving cell ideas, alternative product metal extraction methods, and alternative electrolyte compositions. These tests are conducted in the Seattle laboratory or by subcontractors.

The 200A cell tests serve to validate design ideas, to give 72-to-100 hour anode alloy corrosion data, and to facilitate process control development. Tests of this type are conducted in both the Seattle, WA laboratory and the new pilot cell facility at the Northwest Aluminum Company plant in The Dalles, OR. In Seattle, the emphases are consistent with those of the laboratory tests, and the cell specifications change consistently with test objectives. In The Dalles, the 200A cells are design pre-cursors of the 5kA pilot cells, thus of a mostly consistent design.

The metallurgical studies focus upon alloy fabrication, welding, and riser protection. Work is underway in-house to cast anode alloys. Several commercial firms have been contacted and engaged to cast and/or sinter alloys. Additional efforts address treatments of as-cast materials that

may improve the mechanical and corrosion properties. Welding tests are being carried out in-house and by Lawrence Livermore National Laboratory (LLNL). The risers are lengths of alloy that carry current between the external electrical bus and the active anodes immersed in electrolyte. The risers are subject to uniquely corrosive environment, and protection is essential to limit scaling into the electrolyte. Work is underway to develop alternative methods of protecting the risers.

The 5kA cell activity has the objective of fabricating and operating cells of this capacity. The design will incorporate full-sized electrodes such that a commercial cell of, say, 150kA capacity will comprise the same electrodes, but more of them. Additional objectives are refining cell design approaches and testing system components and process control for continuous periods of thousands of hours.

Accomplishments

Laboratory tests

During the year, the laboratory studies made progress in all areas. Additional physical properties measurements made complemented and added to those made earlier in the project. Difficult electrochemical measurements were made. Ongoing anode corrosion characterizations expanded the understanding of corrosion mechanisms and the influences of process conditions. Also, a new method was explored for producing samples for characterization. Additional laboratory work expanded knowledge about the use of alternative low-temperature electrolytes and the impacts of these on anode performance, and addressed several alternative cell construction and product metal removal schemes using 200A cells.

Table 1 lists the physical properties measurements made during the project to-date, and the organizations that made the measurements. The last three entries were generated during the current year. Accordingly, previous information about alumina dissolution rates in some low-temperature electrolytes was verified, and measurements were made with additional types of alumina. The last two entries indicate that the solubilities of anode corrosion products were initiated and completed during the year.

Electrochemical techniques resulted in several accomplishments. The motivations for using these techniques include to gain mechanistic information about processes at the system electrodes, and to explore the possibilities of adapting such methods for process control. Data collected generated Tafel plots. Difficulties encountered by one group were overcome by another, yielding impedance spectra of processes at both

Table 1: Physical properties measured during the project to-date. The organization conducting each type of measurement is listed.

Property Measured	Organization
Vapor Pressure	NTNU[1] Institute of Chemistry
Interfacial Tension between Al and Melt	Institute of Inorganic Chemistry, Bratislava[2]
Alumina Solubility	CSIRO[3]
Alumina Diffusion Coefficient	CSIRO[3]
Alumina Dissolution Rates	SINTEF[4]
Viscosity	Institute of Inorganic Chemistry, Bratislava[2]
Density	Institute of Inorganic Chemistry, Bratislava[2]
Surface Tension	Institute of Inorganic Chemistry, Bratislava[2]
Aluminum Solubility	Dept. of Inorganic Chemistry, Bratislava[2]
Electrical Conductivity	NTNU[1] Dept. Applied Electrochemistry
Alumina Dissolution Rates	SINTEF[4]
Anode Metal Oxide Solubilities	SINTEF[4]
Anode Metal Fluoride Solubilities	SINTEF[4]

[1]Norwegian University of Science and Technology, Trondheim, Norway
[2]Slovak Academy of Sciences, Bratislava, Slovakia
[3]Commonwealth Scientific Industrial Research Organization, Australia
[4]SINTEF Materials

anode and cathode. The hypothesis that resistometry might prove useful in process control was rejected. However, the prototype of a bath composition determination instrument is nearing completion. Work during the year investigated the sensitivity of the instrument to changes in the bath composition in relation to various variables, such as temperature and probe location within a cell.

Anode corrosion characterizations are ongoing. These involve producing specimens by electrolysis tests, then subjecting the specimens to analysis by SEM and microprobe. This approach yields maps of the elemental composition versus surface location and distance perpendicular to the surface. The latter indicates the corrosion depth, and the changes of corrosion products with depth. The data indicates the stoichiometries of the corrosion products. In some cases, these are

corroborated by x-ray diffraction data obtained from the corrosion products.

The corrosion characterizations are used to compare different alloys, and the effects of different process conditions on a given alloy. The corrosion depth and product stoichiometries are supplemented by product metal purity data and cell voltage data to compare different alloys and process conditions.

Many of the specimens are prepared by conducting electrolysis, then removing the specimen anode from the electrolyte, allowing it to cool, and then performing the characterizations. Once the specimen is removed from the electrolyte, however, it is subject to additional corrosion processes in air as it cools. While some of the features of the in-situ corrosion process are not potentially affected by this, others can be. Consequently a new method was adopted to generate some of the specimens.

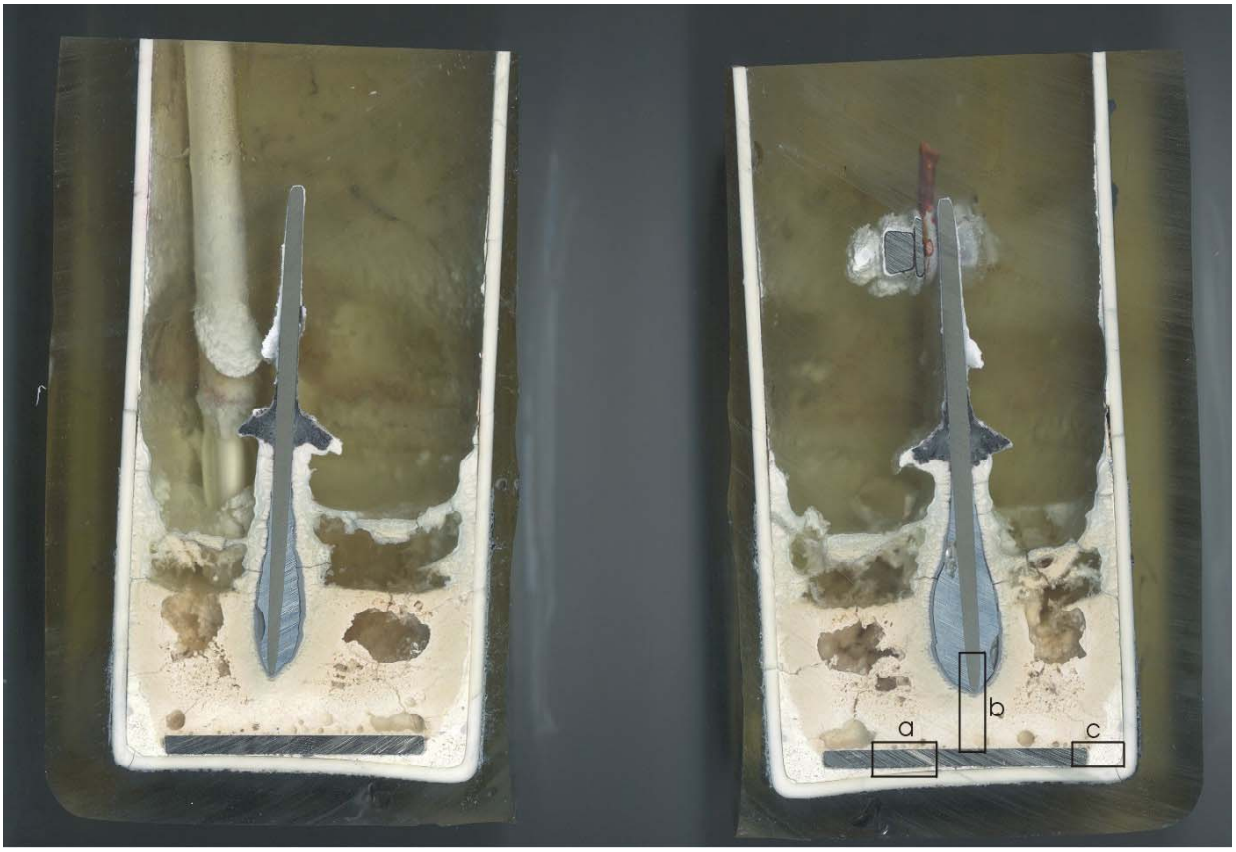
The new method involves freezing the electrolysis cell while electrolysis is maintained. Typical electrolysis tests, described fully elsewhere [1-3], employ a test stand that incorporates external heating. The electrolyte is not kept liquid by the heat generated from electrolysis, but by the external heating. During electrolysis, the current is typically held constant, and the voltage allowed to change as needed. In this new method, a freezing process follows a period of this typical electrolysis. The electrolysis power is switched from constant current to constant voltage, and the external heaters are switched off. Over a period of about fifteen minutes, the test cell temperature drops. As it does so, the electrolyte can begin to freeze. The resistance to electrolysis current increases, so the current drops, until it is essentially zero and the cell contents are all solidified.

After freezing, the anode specimen resides at the bottom of an alumina crucible, covered by frozen electrolyte. The crucible is sectioned using a large circular diamond blade. This exposes a representative section of the specimen anode, which can then be mapped. An example of a sectioned crucible is shown in Figure 1.

Although this method is used to prepare anode specimens, it yields interesting information about the electrolyte, also. A discussion of this aspect by Dr. Craig Brown will be presented at the TMS annual meeting in San Diego on March 5, 2003, and published in *Light Metals 2003*.

Ongoing work continued to study the effects of electrolyte composition on anode corrosion. This has two aspects. One aspect is the effects of

Figure 1: A sectioned frozen cell. The alumina crucible is about 2.5 inches in diameter. The specimen anode is seen on the bottom of the crucible. In the right half of the picture, the areas to be mapped are outlined. In the center, above the anode, the suspended cathode appears. It is a slab of titanium diboride, wetted by the product metal. The drop of product metal collected on this cathode is clearly evident. The decrease in electrolyte volume upon freezing is indicated by noting that the bath level during electrolysis was about halfway up the cathode, and by the voids present in the frozen bath. The alumina sheath in the left-hand section housed a thermocouple.



minor components, such as a few percent calcium fluoride, added to the dominant composition. The other is changes in the formula of the bulk electrolyte. The latter influences the eutectic temperature, and can have a great impact on the width of the composition "operating window." Tests with different electrolytes were conducted in both small, 10A cells, and with 200A cells.

Additional laboratory work focused on expanded the range of alternatives available as the overall system development proceeds. This work included tests to develop alternative methods of product metal removal, of active anode liner design, and cathode fabrication.

Pilot plant

A major accomplishment was the commissioning of a new pilot plant facility in The Dalles, OR. This facility comprises enough space for two 200A cell test stands and at least three 5kA cells, offices and control rooms, a chemistry lab and an x-ray fluorescence (XRF) lab, and a machine shop.

At the end of the project year, nineteen 200A cell tests had been conducted in this facility. Typically, electrolysis is maintained for 72-to-100 hours in these tests. The tests have focused upon verifying cell design ideas, demonstrating dynamic range of operation, and testing anode alloys.

The 200A cells implement a variety of features. These include the best known method of riser protection, continuous alumina feed, and bath composition control maintained using XRF analysis of bath samples. The current efficiencies are typically 90-92% of theoretical, and impurities in the product metal from anode or cathode components fall to within the program targets.

Metallurgical studies

Activity here centered upon investigating treatments of as-cast alloys, and welding. Because of potential patents, not much can be revealed about the former. However, the investigations involved producing treated material, characterizations by SEM, using treated material as test anodes, and some post-electrolysis characterizations with SEM and microprobe methods.

The in-house welding efforts have shown that TIG welding of at least some of the alloys is possible. Several issues complicated this practice. One was choice of the welding wire. Wire of the same alloy to be welded does not yet exist, and is prohibitively expensive to obtain in relatively

small quantities. However, suitable alternatives were found. Another complication was the oxidation of the alloy during welding.

For its part, LLNL is addressing welding, also. At project year's end, the work is just beginning, and is being held back by availability-of-funds issues. A preliminary test was conducted using exotic electron beam welding. Although not a good candidate for a commercial welding process, this method gives a reliable "best case" of weld quality.

5kA cells

Another activity associated with the pilot plant is design and construction of 5kA cells. A design has been completed. The rectifier has been installed and dry tested, and the bus work for one cell installed. The components for the cell and auxiliaries, such as pre-heat ovens, are now on order. An overall process specification, including electrolyte composition, operating temperature, anode and cathode current densities, and so forth has been generated.

The main problem currently in this activity is finding a suitable source of anode material. The vendors that supplied cast material earlier in the program were rejected as sources for the 5kA cell because of material quality issues and price. Efforts continue to expand in-house casting operations to produce pieces of sufficient size and quality. Discussions are in progress to engage additional commercial vendors. Most recently, an attempt is being made to engage Oak Ridge National Laboratory to produce the material for the first 5kA cells.

References

[1] Craig W. Brown, "Laboratory Experiments with Low-Temperature Slurry-Electrolyte Alumina Reduction Cells," *Light Metals 2000* (2000), pp. 391-395.

[2] Craig Brown, "Next Generation Vertical Electrode Cells", *Journal of the Minerals, Metals and Materials Society* (Volume 53, Number 5, May 2001), pp. 39-42.

[3] Craig W. Brown, "Final Report: Wetted Cathodes for Low-Temperature Aluminum Smelting" (Report DOE/ID-13901, UDSOE Office of Industrial Technologies, 2002).

Plans for Next Year:

Many of the activities of the present year will be pursued further in the coming year. This is especially true of the laboratory work, with the main

emphases upon exploring and developing alternative ways to address various aspects of the total system, and upon furthering the fundamental understanding of the process of aluminum electrolysis with nonconsumable anodes.

In the pilot plant, a majority of effort in the coming year will be directed towards commissioning the first 5kA cell. It is anticipated that the first cell may not operate for long, and be followed by a second iteration. Once the design has been qualified, additional cells will be added to the pilot plant cell line.

Patents: The following patents derived from the work have issued to-date:

Craig W. Brown and Theodore R. Beck, *Aluminum Low Temperature Smelting Cell Metal Collection*, U.S. Patent No. 6,419,812 (July 16, 2002).

Craig W. Brown, Theodore R. Beck, and Patrick B. Frizzle, *Cathode Connector for Aluminum Low Temperature Smelting Cell*, U.S. Patent No. 6,419,813 (July 16, 2002).

Craig W. Brown and Patrick B. Frizzle, *Low Temperature Aluminum Reduction Cell Using Hollow Cathode*, U.S. Patent No. 6,436,272 (August 20, 2002).

The following applications have been filed:

Brown, Bergsma	10/126,087	4/22/02
Brown	10/287,029	11/4/02

Milestone Status Table:

The table starts on the following page.

Identification Number	Description	Planned Completion Date	Actual Completion Date	Comments
	Lab Scale Studies			
1.	Evaluate anode alloys with 5-hour tests in 10-ampere cells	1 Jul 1999	18 Jun 2000	Original test matrix was extended
1.1.	Compare electrolysis test data	1 Sep 2003		Ongoing
1.2.	Microscopic examinations of anodes	30 Sep 2003		Ongoing
2.	Continue work on aluminum collection			Work both in laboratory and at pilot plant
2.1.	Determine method of choice for initial pilot plant	31 Aug 2002	31 Aug 2002	See 2. Under Pilot Cell Tests
2.2.	Continue lab tests of alternate/continuous extraction methods	30 Sep 2003		See item 3.2.
3.	Perform 100-hour tests in 200-300 ampere cells	30 Sep 2003		Ongoing in laboratory See also Metallurgical Studies
3.1.	Evaluate alternate cell designs	30 Sep 2003		
3.2.	Research and optimize alternative continuous metal extraction methods	30 Sep 2003		
4.	Electrode process characterizations			Lab work to extend fundamental understanding, not process control
4.1.1.	Electron microscopy with microprobe	30 Sep 2003		Ongoing
4.1.2.	Impedance spectroscopy	31 Dec 2002		Final report by consultant in preparation
4.1.3.	Alumina/electrolyte studies	30 Sep 2003		Ongoing
4.1.3.1.	Alumina dissolution rate determinations	30 Mar 2003		First pass completed, second phase underway
4.1.3.2.	Impact of alternate bath compositions	30 Sep 2003		Ongoing
4.1.3.3.	Impact of low-level bath components	30 Sep 2003		Ongoing
5.	Evaluate test results	30 Sep 2003		

5.1.	Develop models	30 Sep 2003		
5.1.1	Process/design models	30 Aug 2003		Initial phase completed by consultant
5.1.2	Electrochemical	30 Sep 2003		Ongoing
5.2	Correlate model with cell test data	30 Sep 2003		Ongoing
6.	Evaluate cathodes	30 Sep 2003		Ongoing
	Pilot Cell Tests			
1.	Choose anodes and fabrication method for 5000 ampere cells	30 Sept 2002	31 Oct 2002	Anode composition decided. Cast in sand molds.
2.	Choose aluminum removal method for 5000 ampere cells	31 Aug 2002	31 Aug 2002	Conventional vacuum tapping
3.	Devise alumina feed method for 5000 ampere cells	31 Aug 2002	30 Jun 2002	Continuous screw feeder
4.	Install support systems	31 Jan 2003		To be completed with first 5kA cell
4.1.	Power supply	31 Aug 2002	31 Aug 2002	5kA rectifier installed & dry tested
4.2.	Data collection	31 Jan 2003		To be completed with first 5kA cell
4.3.	Alumina feed	31 Jan 2003		For first cell only
4.4.	Scrubber	31 Jan 2003		For first cell only
4.5.	Process control	31 Jan 2003		For first cell only.
4.5.1.	Fluoride probe	30 Sep 2003		Prototype delivered by consultant in next quarter
4.5.2.	Impedance spectroscopy	30 Sep 2003	15 Dec 2001	Approach abandoned for process control
4.5.3.	Resistometry	30 Sep 2003	15 Dec 2001	Approach abandoned for process control
4.5.4.	XRF	31 May 2002		15 Jul 2002
4.5.5	Other			

4.6.	Aluminum removal	31 Jan 2003		To be completed with first 5 kA cell
5.	Fabricate first 5000 ampere cell	31 Jan 2003		
5.1.	Finalize design	31 Aug 2002	31 Aug 2002	
5.2.	Order components	30 Sept 2002		On-going, multiple items, long-lead items first
5.3.	Final construction	31 Jan 2003		
6.	Initial testing of 5000 ampere cell	9 Feb 2003		Planned start of electrolysis
6.1.	Heat up	7 Feb 2003		
6.2.	Polarization	9 Feb 2003		
6.3.	Metal extraction	10 Feb 2003		Daily after startup
6.4.	Cell shutdown	***		Decision to be based on cell performance
7.	Evaluate 5000 ampere cell operation	3 Mar 2003		Three-week stabilization period
7.1.	Evaluate operation results	10 Feb2003		On-going following startup
7.2.	If necessary, modify design and repeat Tasks 1-6	3 Jun 2003		Assuming necessity apparent at evaluation of operation results
8.	Implement additional 5000 ampere cells	15 Dec 2003		Six months after confirmation of correct designs
8.1.	Replicate best design	15 Dec 2003		
8.2.	Continuous operation of pilot cell line	15 Dec 2003		Continuous operation will commence with first successful cell, may be 9 Feb 2003.
	Metallurgical Studies			
1.	Evaluate anodes with 75 to 200 72-hour 300 ampere cell tests	23 Aug 2003		Based on 75 tests, starting mid-March 2002
1.1.	Fabricate alloy anodes	9 Aug 2003		Fabrication on-going with tests

1.1.1.	Cast anodes from Northwest Aluminum Technologies and outside contractors	9 Aug 2003		
1.1.2.	Sintered anodes from outside contractors	9 Aug 2003		
1.1.3.	As 1.1.1. with 0.5 and 2% carbon	9 Aug 2003		
1.1.4.	As 1.1.1. with alloy homogenization	9 Aug 2003		
1.2.	Characterize anodes prior to cell testing	9 Aug 2003		On-going with each anode fabrication
1.3.	Collect cell test data	23 Aug 2003		On-going with each test run
1.4.	Post-test characterizations	30 Sept 2003		On-going with each test run
2.	Alloy welding evaluations	31 Jan 2003		Needed for 5kA cell construction
2.1.	Evaluate welding methods	31 Jan 2003		
2.1.1.	High power laser	30 Sep 2003		Preliminary study in progress by LLNL
2.1.2.	Electron beam	30 Sep 2003		Preliminary study in progress by LLNL
2.1.3.	TIG	31 Jan 2003		LLNL awaiting funds release
2.2.	In-service tests of anode welds	3 Jun 2003		Awaiting results of in-house and LLNL tests
3.	Anode riser protection studies	30 Nov 2002	31 Oct 2002	Concluded for 5kA cell construction
3.1.	Evaluate ceramic materials	31 Aug 2002	31 Aug 2002	Concluded for 5kA cell design Ongoing work on alternatives
3.2.	Evaluate protective coatings	31 Aug 2002	31 Aug 2002	Concluded for 5kA cell design Ongoing work on alternatives

Budget Data (as of 9/30/02):

Phase / Budget Period			Approved Spending Plan			Actual Spent to Date		
			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	9/17/98	9/16/00	724,915	310,678	1,035,593	776,328.45	332,712.19	1,109,040.64
Year 2	9/17/00	9/16/01	901,842	386,504	1,288,346	815,943.50	349,690.07	1,165,633.57
Year 3	9/17/01	9/30/02	2,898,438	1,272,172	4,170,610	1,204,615.36	516,263.73	1,720,879.09
Year 4								
Year 5								
		Totals	3,606,833	1,545,786	5,152,619	2,796,887.30	1,198,665.99	3,995,553.30

Spending Plan for the Next Year:

Month	Estimated Spending
Should be completed for each month of the next year	
October 2002	$150,920
November 2002	$150,920
December 2002	$150,920
January 2003	$155,448
February 2003	$155,448
March 2003	$155,448
April 2003	$158,466
May 2003	$158,466
June 2003	$158,466
July 2003	$161,484
August 2003	$161,484
September 2003	$161,484